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TOWARDS AN ENVIRONMENTAL STANDARD FOR THIOSALT EFFLUENTS

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TOWARDS AN ENVIRONMENTAL STANDARD FOR THIOSALT EFFLUENTS

by

E. Rolia*

ABSTRACT

Environmental standards for thiosalts are likely to be based on the pH produced by their total oxidation and assuming that minimal dilution of the effluent occurs in the receiving watercourse. Under these conditions, a maximum of 10 mg/L thiosalts can be tolerated if the initial pH ~10 and the final pH on oxidation is to be no lower than 5. If an initial pH ~11 is acceptable for discharge, a maximum of 60 mg/L thiosalts can be tolerated while yielding a final pH on oxidation ~5. These concentration limits nearly equal the values calculated from the theoretical pHs produced by the acid formed on complete oxidation of the thiosalts. Slaked lime and sodium hydroxide yield similar pH-thiosalt relationships, and both synthetic and real effluents were found to behave similarly. A procedure for determining the initial pH required to neutralize all the potential acidity generated by the oxidation of any concentration of thiosalts is also presented.

Acceptable discharges will contain low thiosalt concentrations and the analytical procedures for low thiosalt levels have been verified.

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The standard mercuric chloride titration procedure for thiosalts is useful to the 5 mg/L level with an accuracy of ∿5%; the relative error (1σ) drops to <1% for thiosalt concentrations >50 mg/L. The limit of thiosalt detection is ∿1 mg/L.

INTRODUCTION

Thiosalts ($S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, etc.) are generated during the milling of sulphide ores in alkaline media; the extent of generation is especially severe when massive sulphide ores are processed (1). Thiosalts are only partially oxidized in many tailings/biostabilization ponds, and they are not destroyed by conventional liming procedures which precede discharge to the water systems. Hence, thiosalts can be discharged from milling operations, and their presence in rivers or lakes is objectionable by virtue of the acid formed on their eventual oxidation. Thiosalts themselves do not appear to be injurious; it is only the acid formed on their oxidation that creates problems.

Surprisingly, there is currently no specified maximum thiosalt concentration for the safe discharge of thiosalt-bearing effluents although acceptable pH ranges are provided (2). The setting of a thiosalt specification is complicated by the high ionic strength of many milling effluents that may preclude a simple conversion of potentially generated acid concentration to pH and by the pre-liming of the effluent before discharge that provides some residual buffering capacity. The whole problem is further complicated by some uncertainties in the analytical procedures for the low thiosalt concentrations (<100 mg/L S_2O_3) involved.

Within such a framework, it seemed desirable to define, using effluents similar to those encountered in industrial practice, the ultimate pH which could be produced by the complete oxidation of a known quantity of thiosalts with a given degree of preneutralization. These data together with environmentally acceptable pH ranges should lead directly to a thiosalt specification where no dilution occurs in the receiving watercourse. Where dilution does occur, it should be a fairly simple matter to adjust the

ultimate pH value for the change in volume encountered under various flow conditions. A further objective of this study was to assess the accuracy of the mercuric chloride titration procedure for the low thiosalt concentrations likely to be encountered in environmentally acceptable discharges. The results of both investigations are summarized in this report.

EXPERIMENTAL

Total thiosalts were determined, as thiosulphate, by the acidimetric titration of the acid formed by the mercuric chloride oxidation of the thiosalts (1,3,4). The titration was carried out to pH 4.30 using a Metrohm Herisau automatic titrator with a 20 mL delivery pipette and model EA 120 glass electrode. All reagents were purchased analytical grade chemicals, except for $K_2S_3O_6$ which was synthesized in the laboratory (1). Sodium hydroxide solutions were made from CO_2-free water and were stored in tightly sealed bottles after preparation.

Previous work (5) has shown that the tailings effluent from Brunswick Mining and Smelting Corporation (BMS) Bathurst, New Brunswick contains, in mg/L: $S_2O_3^{2-}$ 900, SO_4^{2-} 674, Cl^- 598, Ca^{2+} 473 and Na 360. Excluding the thiosalts, these compositions are approximately equal to 5 mmol/L Na_2SO_4, 5 mmol/L $CaSO_4$ and 8 mmol/L $CaCl_2$. These compositions are felt to be more or less typical of many milling circuits, and it was therefore decided to carry out the test work using synthetic solutions with this background composition. This practice should compensate for any buffering/activity/precipitation effects likely to be seen with real effluents. In addition, a few confirmatory tests were also done with real effluents from BMS, and these data agreed closely with the results from the synthetic effluents.

Since the purpose of this investigation was to determine the pH of the effluent upon complete thiosalt oxidation for various initial levels of thiosalts and preneutralization, the experimental procedure consisted of dissolving an accurately weighed quantity of thiosalt in the background solution, adjusting the initial pH to simulate effluent liming, oxidizing the thiosalts to sulphate with H_2O_2 and finally remeasuring the solution pH after complete thiosalt oxidation. The exact procedure consisted of the preparation of 1 L of background solution having a known thiosalt concentration. Seven 100 mL samples of this solution were then adjusted to pH 5.20, 10.20, 10.50, 10.80, 11.10, 11.40 and 11.70 using H_2SO_4, NaOH or $Ca(OH)_2$. One mL of 30% H_2O_2 for each 200 mg/L $S_2O_3^{2-}$ was then added to oxidize the thiosalts. The solution was allowed to stand for 30 min at room temperature, and then was boiled for ~30 min. Preliminary test work showed that this procedure was adequate to oxidize all the thiosalts present in this volume of solution. Although residual H_2O_2 did not interfere significantly with the acid determination, it must, of course, be eliminated prior to the mercuric chloride determination of residual thiosalts. It was demonstrated that residual H_2O_2 was destroyed by boiling while using vigorous stirring to prevent bumping which is especially severe in acidic media. The volume of the cooled solution is then adjusted to the original value (100 mL sample plus volume of reagent used to adjust pH) and the resulting pH is measured.

An additional objective of this study was to evaluate the mercuric chloride titration procedure for the very low thiosalt concentrations (0-100 mg/L) that are likely to be permissible for discharge. The following sample sizes in a total 60 mL titrant volume were used.

- 0-50 mg/L as $S_2O_3^{2-}$, 50 mL aliquot,
- 50-200 mg/L as $S_2O_3^{2-}$, 25 mL aliquot,

- 200-500 mg/L as $S_2O_3^{2-}$, 10 mL aliquot,
- 500-1000 mg/L as $S_2O_3^{2-}$, 5 mL aliquot,
- 1000-2000 mg/L as $S_2O_3^{2-}$, 2 mL aliquot.

The solutions were titrated with 0.005 N NaOH to the pH 4.30 end point using the standard mercuric chloride procedure (1). The total thiosalts were calculated using the equation:

$$\text{mg/L as } S_2O_3^{2-} = 56000(V_t + V_b)\frac{N}{A}$$

where V_t and V_b are the volumes (mL) of sodium hydroxide solution (N normality) used for the sample and blank titrations, respectively, and A is the volume (mL) of the sample. A number of replicate samples were analyzed to yield the mean concentration and the statistical reliability of the method for different thiosalt concentrations.

RESULTS AND DISCUSSION

ANALYSIS OF LOW THIOSALT CONCENTRATIONS

Since an accurate analytical method for low thiosalt concentrations is an essential part of both this investigation and any commercial thiosalt control strategy, this aspect of the program was investigated first. Replicate determinations for a weighed amount of thiosulphate in the background solution were made using the mercuric chloride titration procedure (1), and the results are shown in Table 1.

Table 1. Statistical results of the analysis of 50 mL of thiosulphate solution by acidimetric titration to the pH 4.30 end point.

Taken $S_2O_3^{2-}$ mg	Conc. $S_2O_3^{2-}$ mg/L	Number of determinations	Average mg	Standard deviation mg	Relative standard deviation, %
0.28	5.6	8	0.28	0.016	5.6
2.24	44.8	8	2.20	0.024	1.1
5.60	112.0	8	5.51	0.028	0.5

The procedure is accurate at the 45 mg/L S_2O_3 level and is fairly accurate (~5% relative standard deviation) even at the 5 mg/L S_2O_3 range. Replicate determinations were also made in the absence of thiosulphate (blank determination) and the standard deviation was 0.2 mg/L S_2O_3. According to Kirchmer (6) the limit of detection is 4.65 x standard deviation for the blank, suggesting a ~1 mg/L $S_2O_3^{2-}$ detection limit for the mercuric chloride titration procedure. The mercuric chloride analytical procedure seems sufficiently accurate and sensitive to monitor a thiosalt control strategy.

pH RESULTING FROM THE OXIDATION OF THIOSALT EFFLUENTS

Figure 1 shows the final solution pH resulting from the H_2O_2 oxidation of various concentrations of S_2O_3 in simulated BMS effluent whose initial pH was adjusted to different levels with NaOH to simulate pre-liming of the effluent. The graphs are essentially titration curves of the base added to the solution and the acid generated by thiosulphate oxidation. For a given degree of preneutralization the final pH drops progressively with increasing thiosalt concentration, and higher initial pH values would allow a more concentrated thiosalt effluent to be discharged while still

ensuring a specified pH in the fully oxidized effluent. The corresponding data for trithionate are given in Figure 2; tetrathionate decomposes rapidly in alkaline media to trithionate and thiosulphate, and the data for this thiosalt are given in Figure 3.

Preliminary work established that H_2O_2 readily oxidized all thiosalts present in <u>basic</u> solutions, and it is known that oxidation by H_2O_2 yields the same amount of acid as oxidation by O_2 that would occur in the environment.

$$S_2O_3^{2-} + 2O_2 + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ \quad (1)$$

$$S_3O_6^{2-} + 2O_2 + 2H_2O \longrightarrow 3SO_4^{2-} + 4H^+ \quad (2)$$

$$S_4O_6^{2-} + 7/2\ O_2 + 3H_2O \longrightarrow 4SO_4^{2-} + 6H^+ \quad (3)$$

$$S_2O_3^{2-} + 4H_2O_2 \longrightarrow 2SO_4^{2-} + 3H_2O + 2H^+ \quad (4)$$

$$S_3O_6^{2-} + 4H_2O_2 \longrightarrow 3SO_4^{2-} + 2H_2O + 4H^+ \quad (5)$$

$$S_4O_6^{2-} + 7H_2O_2 \longrightarrow 4SO_4^{2-} + 4H_2O + 6H^+ \quad (6)$$

In <u>acid</u> solutions, the rates of the above reactions are greatly reduced and competitive reactions can occur. Attempts to use Cu or Fe catalysts (7) were not successful as these produced pH changes during precipitation at modest pH values. After some experimentation, it was found that thiosalts could be completely oxidized in acid solutions when:

(1) a stoichiometric excess of H_2O_2 was added

(2) low concentrations of thiosalts (0.01-0.4 mmol $S_2O_3^{2-}$/100 mL) were oxidized

(3) the solution was boiled for ~30 min,

and these procedures were incorporated into the preferred technique.

The 0 mg/L thiosalt values shown on Figs. 1-3 were obtained after the addition of the H_2O_2, are not the same as the initial pHs reported in the figure captions that were measured before the peroxide addition. These slight discrepancies arise because H_2O_2 in the presence of dissolved salts acts as a weak base in acid solution and as a weak acid in alkaline media. The modest effect of H_2O_2 on the final solution pH, after reaction and boiling, is illustrated in Table 2 where it can be seen that the effect is most pronounced in near neutral media.

Table 2. Effect on the final pH of the addition of 1 mL of 30% H_2O_2 to 100 mL of synthetic effluent initially adjusted to different pH values. The volume of 0.1 N NaOH used to adjust the pH is given in the first column.

Added 0.1 N NaOH mL	Initial pH	After treatment with H_2O_2 Final pH
-	5.00	5.30, 5.27, 5.17
0.28	10.20	9.60, 9.58
0.55	10.50	10.06, 10.07, 9.96
0.97	10.80	10.41, 10.50, 10.46
1.90	11.10	10.74, 10.88, 10.88
3.70	11.40	11.17, 11.27, 11.12
7.80	11.70	11.44, 11.50, 11.46

According to Environmental Protection Service (2) guidelines, the minimum desirable pH for discharge of undiluted effluent to a waterway is 6.0; the maximum desirable pH is 8-9. Although no specific upper pH limit actually has been regulated, mine operators are cautioned to avoid discharge of effluents with high pH's. It would appear that the most favourable

situation which the industry could expect would be discharge of a pH ∿11 effluent containing thiosalt concentrations only sufficient to lower the pH to ∿5.0 in undiluted effluent. Examination of Figs. 1-3 suggests that the effluent would have to contain <60 mg/L thiosalts to satisfy these initial and final constraints on pH.

Equations 4-6 indicate the theoretical amounts of acid produced during thiosalt oxidation by H_2O_2 and the experimental results obtained using synthetic effluent closely approximate these values. Figure 4 compares the measured initial pH required to achieve a pH 7.0 effluent on complete oxidation of various concentrations of thiosulphate, trithionate or tetrathionate versus the calculated pH for similar concentrations. It is clear that all the thiosalt species can be described by a single curve and that, for a given thiosalt concentration, the measured and calculated initial pH's to yield a neutral effluent on complete thiosalt oxidation do not differ significantly. Real effluents will likely permit a slightly higher thiosalt concentration than calculations would suggest. Thus, the acid concentrations produced by the complete oxidation of a thiosalt effluent can be readily calculated and converted to estimate the final pH of the solution. A set of typical calculations is given in Table 3. The "Calc. Final pH" is the calculated pH based on the acid produced by total thiosalt oxidation and assuming that the effluent was initially neutral. The "Required pH of Effluent" is the pH to which the solution would have to be raised initially to ensure complete neutralization of all the acid formed by the oxidation of the thiosulphate. These pH values are calculated and ignore the slight activity/buffering effects operative in these solutions (Fig. 4). The data suggest that only very low thiosalt concentrations can be tolerated if the initial effluent pH is <11. Dilution of the effluent in the receiving

stream would permit a higher initial pH to be used, but the mixing in the receiving watercourse would have to be rapid and thorough to prevent locally high alkalinity values. Figures 1-4 suggest that an initial effluent pH of ∿11 would be adequate to neutralize the acid produced by ∿60 mg/L thiosalts, and assuming no dilution of the solution.

Table 3. Theoretical drop in pH produced by the oxidation of thiosulphate and the theoretical pH of effluent discharge required to neutralize the potential acidity.

Conc. $S_2O_3^{2-}$ mg/L	Conc. $S_2O_3^{2-}$ mmol/L	Conc. H^+ mol/L	Calc. Final pH	Required pH of effluent
0.5	0.00445	0.0000089	5.05	8.95
1.0	0.0089	0.000017	4.75	9.25
1.75	0.015	0.000031	4.5	9.5
3.5	0.031	0.000062	4.2	9.8
7	0.062	0.000125	3.9	10.1
14	0.125	0.00025	3.6	10.4
28	0.25	0.0005	3.3	10.7
56	0.5	0.001	3.0	11.0
112	1.0	0.002	2.7	11.3
224	2.0	0.004	2.4	11.6

USE OF LIME FOR NEUTRALIZATION

Commercial effluent treatment operations are likely to be based on slaked lime ($Ca(OH)_2$) rather than NaOH which is easier to use for laboratory studies. Both reagents were found to yield similar results. Preliminary work was done with a synthetic effluent containing 1.9 mmol S_2O_3/L at pH 6.13. This was oxidized with H_2O_2 to give a solution at pH 2.60 which was then

neutralized with the same number of equivalents (0.378) of either NaOH or $Ca(OH)_2$. For both reagents, the final pH was 8.2, suggesting that effluent discharge pH standards will be independent of the alkalinity reagent employed. This point is further illustrated in Figure 5 which shows a comparative set of results for thiosulphate oxidation in synthetic effluents whose initial pH was adjusted to 11.10 by either $Ca(OH)_2$ or NaOH. Within experimental error, the two sets of data are identical, confirming that the type of alkalinity reagent has only a minimal effect on the final pH resulting from the oxidation of moderate concentrations of thiosalts. Thus it would seem that the results realized in this study with NaOH would be applicable to commercial operations based on $Ca(OH)_2$. A limited number of tests were also done using actual effluent from BMS as opposed to the synthetic effluents employed for the majority of experiments. The real effluent contained 1085 mg/L Ca^{2+}, 1800 mg/L SO_4 and 522 mg/L thiosalts as well as traces (<1 mg/L) of Cu, Zn and Pb. The thiosalts were totally oxidized by the H_2O_2 and the resulting pH values were those expected based on the work on the synthetic effluents.

DETERMINATION OF THE INITIAL pH REQUIRED TO NEUTRALIZE ALL POTENTIAL ACIDITY IN A THIOSALT EFFLUENT

A simple procedure was developed to determine the required initial pH of a thiosalt-bearing effluent which contains sufficient base to neutralize all the acidity formed on complete oxidation of the thiosalts. A sample of the effluent is completely oxidized with H_2O_2 to produce an acidic solution. This is then titrated with fairly concentrated base ($\sim$0.1 M NaOH) to the neutral point, and the volume of base is recorded. This same volume of base is then added to a second aliquot of the thiosalt-bearing effluent and the pH is measured. The pH value is then adjusted for the small volume of base added to the original volume of effluent:

$$[H^+] = 10^{-pH} \quad (7)$$

$$[H^+]_{corrected} = [H^+] \times \frac{V_{sample}}{V_{Base} + V_{Sample}} \quad (8)$$

$$pH_{corrected} = -\log[H^+]_{corrected} \quad (9)$$

Because of the logarithmic relationship involved, the volume correction on pH is usually minor and could likely be ignored if concentrated base (>0.1 M) was used; e.g., for 10 mL of 0.1 M NaOH added to 100 mL of sample, the required initial pH was increased from 11.75 to only 11.79. This procedure has been shown to be applicable to both synthetic and real BMS effluents.

CONCLUSIONS

1 - The mercuric chloride titration procedure for thiosalts has been shown to be effective to the 5 mg/L thiosalt range with a relative error decreasing from 5% at 5 mg/L to <1% at 50 mg/L.

2 - If the effluent pH values cannot fall below 5.0, then 10 mg/L thiosalts can be safely discharged at an initial pH 10, and 60 mg/L thiosalts at initial pH 11.

3 - Slaked lime and sodium hydroxide both yield the same pH-thiosalt concentration relationships.

4 - Small changes in effluent volume during analysis (or on discharge) have only a small effect on the permissible pH ranges.

5 - A simple oxidation-titration procedure is described to determine the initial pH required to neutralize all the potential acidity in an effluent having any thiosalt concentration.

6 - Because of the low thiosalt concentrations tolerable in weakly limed effluents, nearly complete destruction of thiosalts will be required prior to their discharge.

ACKNOWLEDGEMENT

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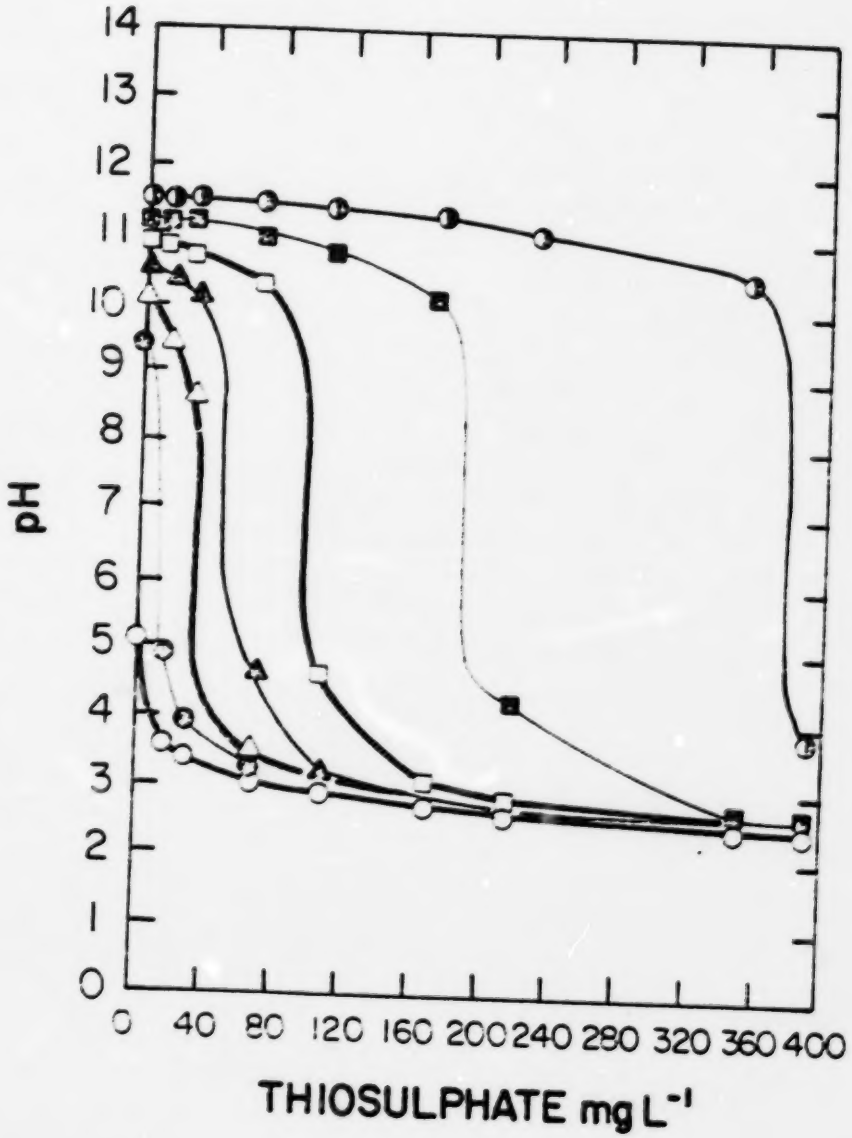
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THIOSULPHATE mg L⁻¹
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2
3
4
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6
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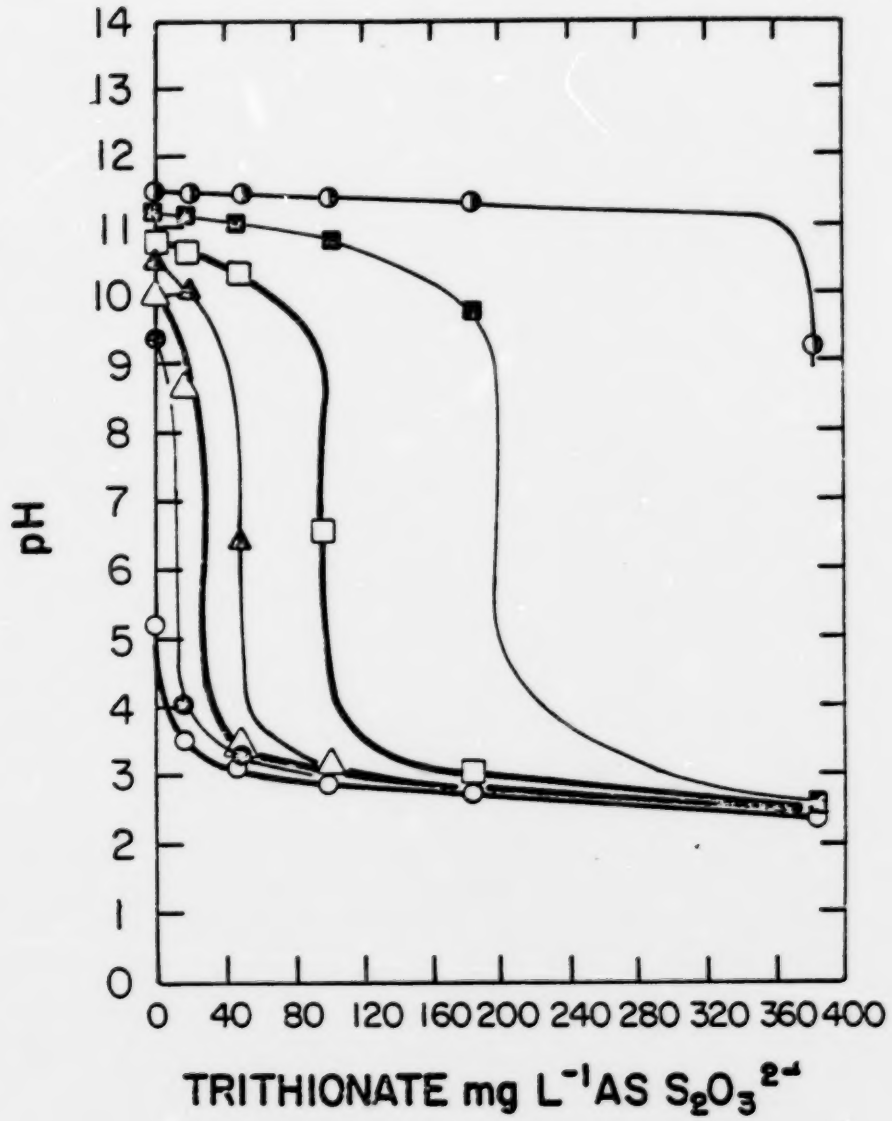

Fig. 2 - Drop in pH resulting from the oxidation by H_2O_2 of different concentrations of trithionate.

Initial pH: ◔ 11.7; ◩ 11.4; ◻ 11.1; ▲ 10.8; △ 10.5; ● 10.2; ○ 5.2.

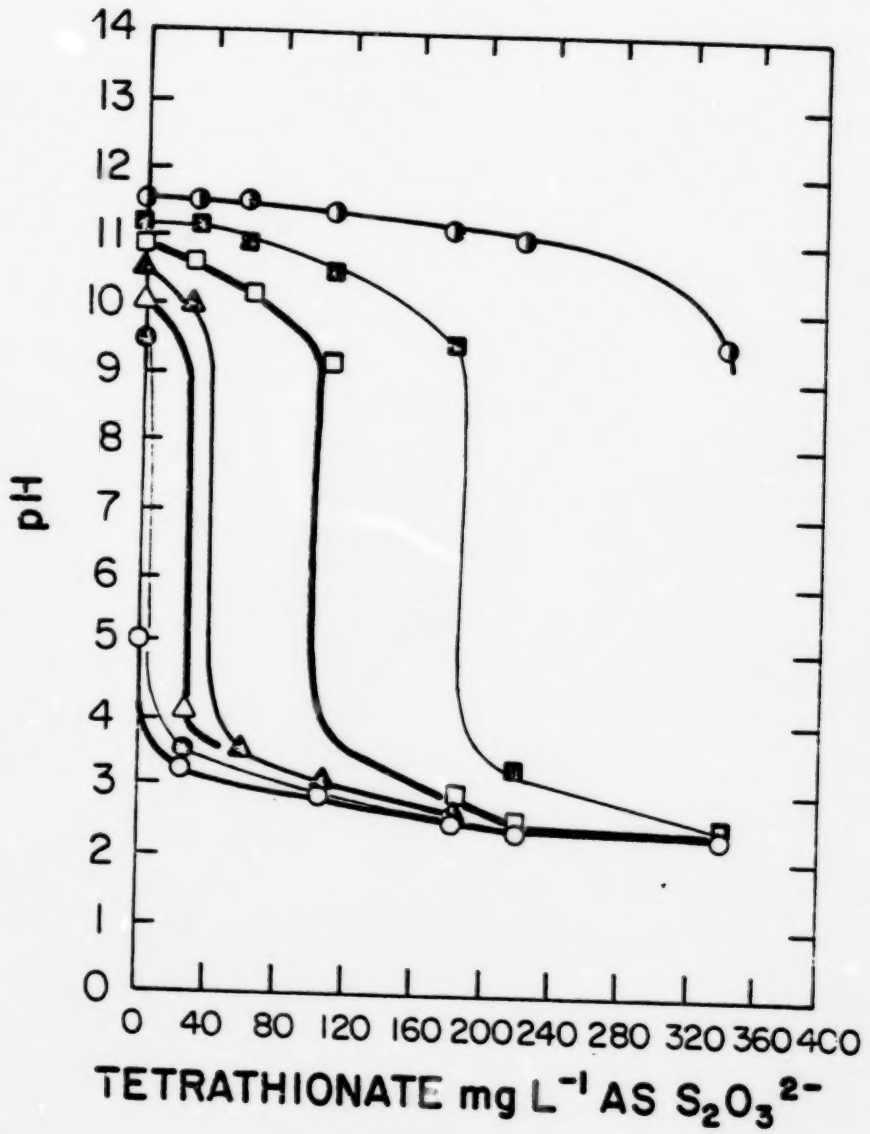

Fig. 3 - Drop in pH resulting from the oxidation by H_2O_2 of different concentrations of tetrathionate.

Initial pH: ● 11.7; ■ 11.4; □ 11.1; ▲ 10.8; △ 10.5; ○ 10.2; ○ 5.2.

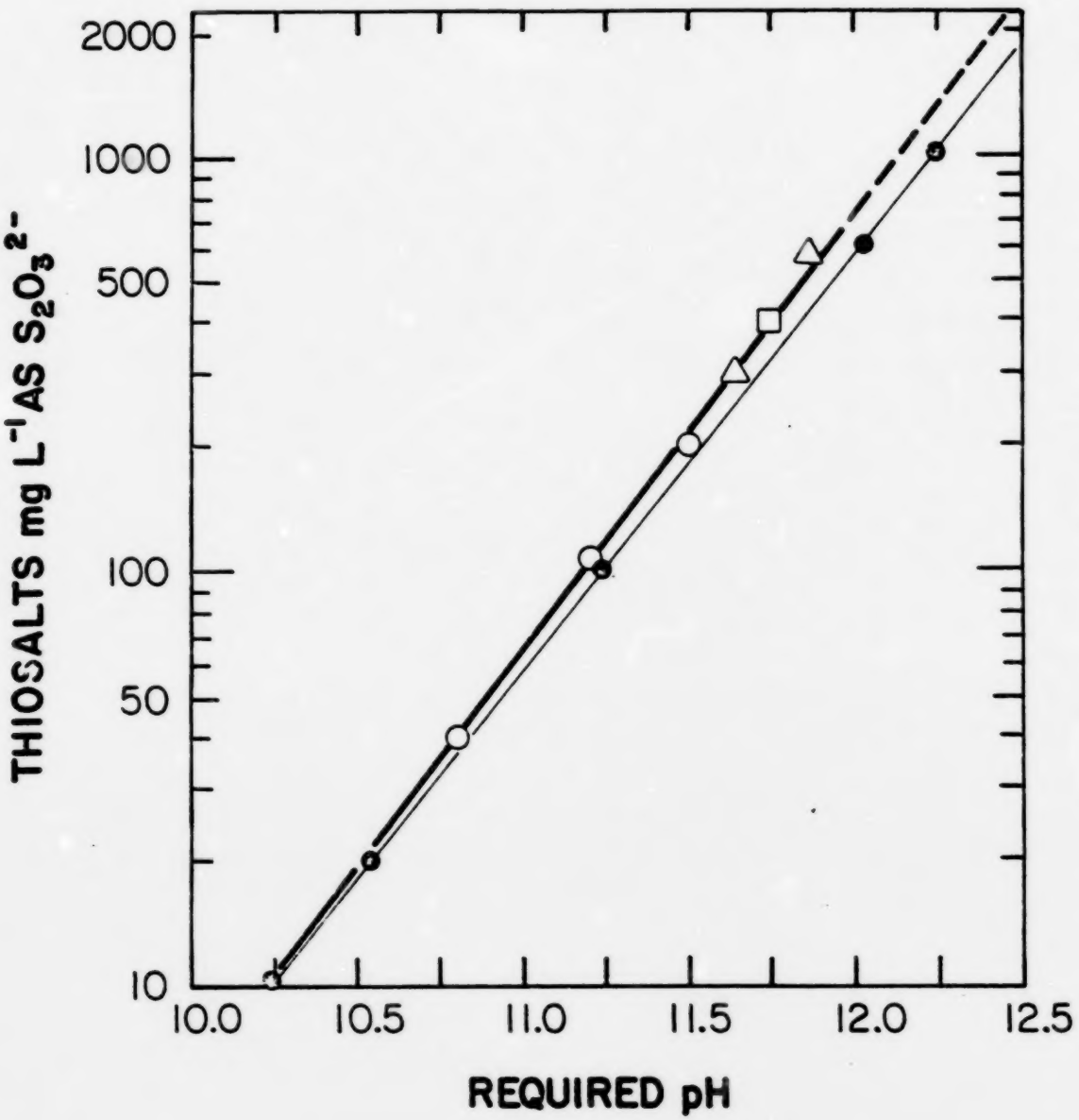

Fig. 4 - Relationship between thiosalt concentration in effluent and the required initial pH sufficient to neutralize the potential acidity to pH 7.0.

Experimental: ○ thiosulphate △ trithionate; ⊏ tetrathionate; ● calculated.

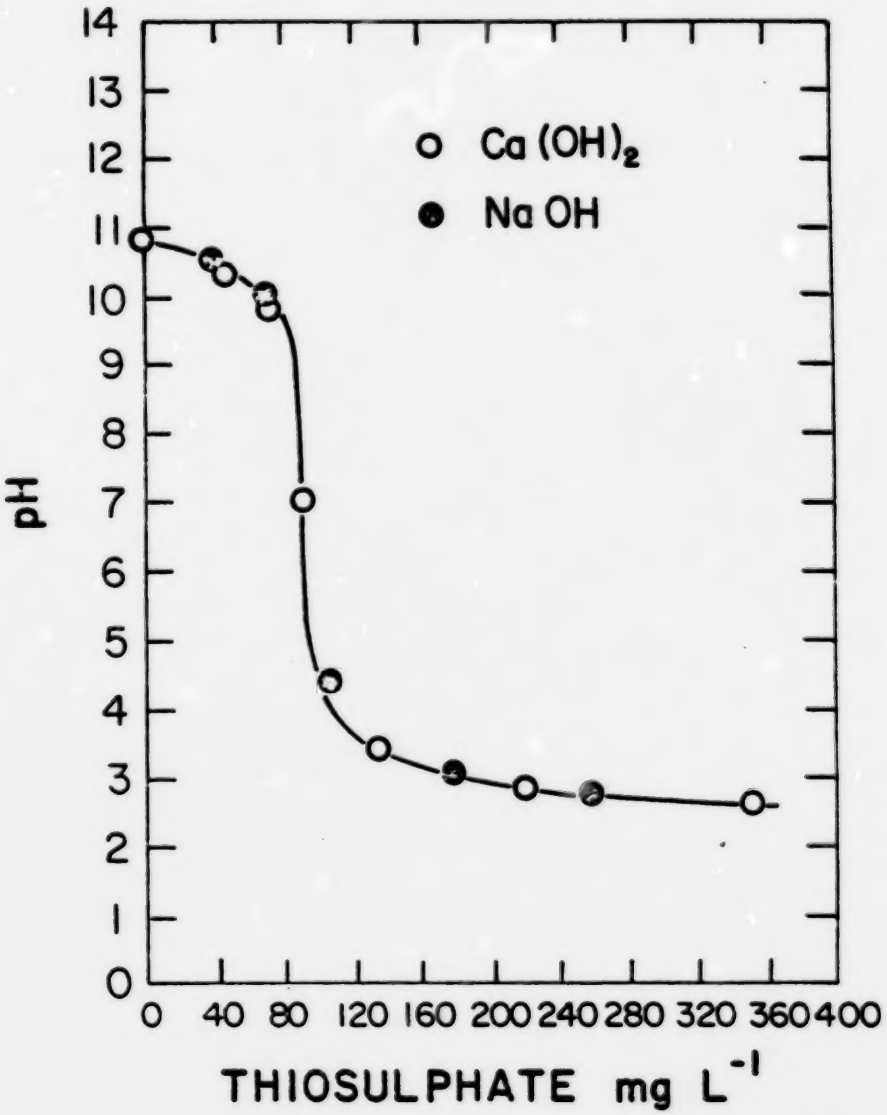

Fig. 3 - The drop in pH due to the oxidation by H_2O_2 of different concentrations of thiosulphate in a synthetic effluent made basic to pH 11.0 by either $Ca(OH)_2$ or NaOH.

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